

LOW TEMPERATURE OXYGEN GAS SENSOR

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REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Patent 15 Application Nos. 60/094,721 filed on July 30, 1998 and 60/123,819 filed on March 11, 1999, which are both hereby incorporated by reference in their entirety.

BACKGROUND

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The present invention relates to sensing devices and the manufacture thereof, and more particularly, but not exclusively, relates to a ferroelectric oxygen gas sensor and a process for manufacturing ferroelectric devices.

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Oxygen gas sensors have a wide range of applications in combustion engine and metallurgical processes. The most notable is their use in modern automobile engine operation and control. The sensor measures the oxygen content in the exhaust of the internal combustion engine and adjusts the air-fuel ratio, accordingly. This regulation process 30 has been found to significantly enhance economical operation and environmental control of combustion engines.

Two types of oxygen sensors are commonly used in the auto industry: the potentiometric type, using zirconia based ceramics such as cubic-stabilized zirconia (CSZ) and the resistive type, using titania (TiO_2). A CSZ potentiometer type sensor requires a porous metal electrode and a reference gas at the reference electrode. A high emf develops across the electrodes as the oxygen partial pressure at the sensing electrode varies or changes in comparison to the reference gas at the reference electrode.

5 Furthermore, the sensing mechanism is a thermally activated process, which requires that the sensor be operated at a temperature higher than 10 300°C in order to register a significant output voltage. This is usually accomplished by positioning the sensor in a hot exhaust gas stream or by heating the sensor using an electric heater. Resistive titania sensors, on the other hand, do not require a reference gas, but do require a tip 15 temperature $\geq 350^\circ C$ for sensor activation. Titania sensors also exhibit strong temperature dependence and require compensation for temperature variations.

Other types of solid-state oxygen sensors using LaF_3 and nonstoichiometric perovskite thin films have recently been reported. Unlike CSZ and TiO_2 sensors, the LaF_3 sensors operate at ambient temperatures, 20 but they suffer from very long response times. Shorter response times of a few minutes were reported by operating the LaF_3 thin films at higher temperatures or by using a special type of a sensitive electrodoping material such as metal phthalocyanine. Sensing capabilities of non-stoichiometric perovskite thin films only appear to have been reported at higher activation 25 temperatures for sensor activation. Thus, the need to develop a low temperature oxygen sensor with a fast response time remains. Furthermore, a low temperature sensor will have a great advantage in a wide variety of applications including medical (life support), biological and environmental applications and process monitoring.

30 The present invention meets such needs, and has other benefits and advantages.

SUMMARY OF INVENTION

The present invention relates to sensing devices, the manufacture and use thereof. Various aspects of the invention are novel, nonobvious, 5 and provide various advantages. While the actual nature of the invention covered herein can only be determined with reference to the claims appended hereto, certain forms and features, which are characteristic of the preferred embodiments disclosed herein, are described briefly as follows.

10 One form of the present includes an oxygen sensor having an operating temperature preferably below about 400K. The temperature is more preferably below about 375K and still more preferably below about 300K. The oxygen sensor includes a nonstoichiometric metal oxide sensor member. Preferably the nonstoichiometric sensing member includes an 15 ionic conductor such as a PZT compound or a yttria stabilized zirconia compound (YSZ).

In another form, the invention includes an oxygen sensor having a 20 graded ferroelectric sensing member. The sensing member may be composed of a $\text{PbZr}_x\text{Ti}_y\text{O}_3$ (PZT) compound, where the ratio of x to y varies in accordance with a predetermined compositional gradient through the sensing member, and the sum of x + y is generally about one. For this type of ferroelectric material, preferably x is in a range of about 0.5 to 0.8, and y is in a range of about 0.2 to about 0.5. More preferably, x is in a 25 range of about 0.55 to about 0.75, and y is in a range of about 0.25 to about 0.45. Instead of PZT, other ferroelectric materials may be utilized in accordance with the present invention, such as $(\text{Ba},\text{Sr})\text{TiO}_3$ (BST), BaTiO_3 , lanthanum-modified PZT (PLZT), and strontium bismuth tantalate (SBT) to name a few.

30 In another form, the present invention includes an oxygen sensor having a non-graded ferroelectric sensing member. The sensing member can be composed of a $\text{PbZr}_x\text{Ti}_y\text{O}_3$ (PZT) compound wherein the sum of x and y is generally about one. Preferably, x is in the range of about 0.5 to

about 0.8, and y is in a range of about 0.2 to about 0.5. More preferably, x is in the range of about 0.55 to about 0.75, and y is in the range of about 0.25 to about 0.45. Similar to the graded ferroelectric sensing member above, PZT can be substituted with other ferroelectric materials.

5 The ferroelectric sensing member can include electrodes formed from any suitable material including, but not limited to platinum, silver, gold, metal phthalocyanine, and metal conductive oxides such as indium-doped tin oxide (ITO) to name a few. The electrodes can be formed using conventional patterning techniques.

10 Another form of the invention includes an oxygen sensing system. This system may be configured to measure oxygen levels in an intake and/or exhaust stream of a vehicle.

15 In still another form of the invention, a manufacturing technique includes: (a) providing a source of ferroelectric material having a first region with a first composition and a second region with a second composition different from the first composition; (b) irradiating a portion of the first region and a portion of the second region with a laser beam to release a mixture from the source with a predetermined ratio of the first composition to the second composition; and (c) forming a layer of a 20 sensing matrix corresponding to the ratio. Irradiation of the source may be performed by scanning a predetermined path along the source with the laser beam to generate one or more plumes of the first and second compositions. Moreover, different amounts of the first and second regions may be scanned in this manner to vary the composition of one or more 25 such plumes. Material released from the source may be accumulated in one or more layers to provide a corresponding ferroelectric device.

30 In a further form, the present invention includes a nonstoichiometric metal oxide sensing member to detect oxygen and a circuit electrically coupled to said sensing member operable to apply an electric field to said sensing member. The sensing member may be comprised of a ferroelectric material such as a PZT or another type of nonstoichiometric metal oxide such as YSZ. The electric field applied to the sensing member

may be of a time varying form, with a peak magnitude of at least about 1 volt per μm .

Still a further form of the present invention includes: providing a nonstoichiometric metal oxide sensing member; applying an electric field to said sensing member; and sensing oxygen with said sensing member. The sensing member may be comprised of a ferroelectric material such as a PZT or another type of nonstoichiometric metal oxide such as YSZ. The electric field applied to the sensing member may be of a time varying form with a peak magnitude of at least about 1 volt per μm .

10 Accordingly, it is one object of the present invention to provide a low temperature oxygen sensing device.

It is another object of the present invention to provide a ferroelectric device.

15 It is still another object to provide a technique to manufacture a ferroelectric device.

Further objects, features, forms, aspects, advantages, and benefits of the present invention will become apparent from the description and drawings provided herein.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagram of a vehicle employing one embodiment of an oxygen sensor in an exhaust gas stream sensor system.

5 Figure 2 is a diagram of a vehicle employing one embodiment of an oxygen sensor in an intake gas stream sensor system.

Figure 3 is a perspective view of a sensing device according to one embodiment of the present invention.

10 Figure 4 is a diagrammatic illustration of one method for depositing a graded ferroelectric material on a substrate.

Figure 5 is a graphical illustration of an Auger depth profile of relative Zr and Ti concentrations for a down-graded film prepared according to the method depicted in Figure 4.

15 Figure 6 is a graphical illustration of (200) peaks as a function of 2θ obtained from x-ray diffraction analysis of PZT 55/45, PZT 75/25 and compositionally graded PZT films.

Figure 7 is a schematic of a Sawyer-Tower circuit coupled to an oscilloscope.

20 Figure 8 is a diagram of an atmosphere and temperature controlled probe station including a specimen stage for analyzing an oxygen sensor prepared according to the method depicted in Figure 4.

Figure 9a is a graphical illustration of the time dependence of the voltage offset for one embodiment of an oxygen sensor having a non-graded ferroelectric film of the present invention.

25 Figure 9b is a graph plotting voltage offset as a function of an applied sinusoidal driving field for one embodiment of an oxygen sensor having a non-graded ferroelectric film of the present invention.

Figure 10a is a graph plotting voltage offset as a function of oxygen concentration for one embodiment of an oxygen sensor having a non-graded ferroelectric film of the present invention.

Figure 10b is a graph plotting voltage offset as a function of oxygen pressure for one embodiment of an oxygen sensor having a non-graded ferroelectric film of the present invention.

5 Figure 10c is a graph plotting voltage offset as a function of temperature for one embodiment of an oxygen sensor having a non-graded ferroelectric film of the present invention.

10 Figure 11a is a graph plotting voltage offset as a series of hysteresis loops as a function of an applied sinusoidal driving field for one embodiment of an oxygen sensor having an up-graded ferroelectric film of the present invention.

Figure 11b is a graph plotting voltage offset as a series of hysteresis loops as a function of an applied sinusoidal driving field for one embodiment of an oxygen sensor having a down-graded ferroelectric film of the present invention.

15 Figure 12 is a graph plotting voltage offset as a function of the log of oxygen pressure for an oxygen sensor having an up-graded ferroelectric film and an oxygen sensor having a down-graded ferroelectric film, which were prepared in accordance with this invention.

20 Figure 13 is a graph plotting the voltage offset as a function of temperature for one embodiment of an oxygen sensor having an up-graded film of the present invention.

Figure 14 is a graph plotting voltage offset as a function of $\text{Log}[\text{pO}_2/\text{atm}]$ of a YSZ film prepared according to the present invention.

25 Figure 15 is a graph plotting voltage offset as a function of the applied sinusoidal driving frequency for a YSZ film prepared according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

For the purpose of promoting an understanding of the principles of the invention, reference will now be made to the embodiments illustrated in the drawings and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended. Any alterations and further modifications in the described device and methods, and any further applications of the principles of the invention as described herein are contemplated as would normally occur to one skilled in the art to which the invention relates.

One embodiment of the present invention is an oxygen sensor having a variety of uses, most notably for use in sensing systems for combustion engines to measure the oxygen levels in an exhaust gas stream and/or an intake gas stream. This oxygen sensor comprises a sensing member made of either a graded or non-graded ferroelectric or other nonstoichiometric metal oxide. At least two electrodes are attached to the sensing member in spaced a part relationship from one another to provide a sensing device akin to a capacitor. When the resulting capacitor device is subjected to an applied electrical driving field, the capacitor exhibits a voltage offset under selected conditions. The magnitude of the voltage offset is dependent upon the gaseous oxygen concentration to which the device is exposed.

Oxygen sensors of the present invention can be used to enhance the efficient operation and environment or pollution control of combustion engines. Figure 1 is a diagram of a vehicle 10 having a combustion engine 12 employing sensing system 14. Sensing system 14 includes oxygen sensor 18 positioned in exhaust line 16 and operably coupled to control circuit 20. Circuit 20 may include a means to provide a driving electric field for application to sensor 18 to generate a voltage offset corresponding to oxygen level. Such driving means are more fully discussed hereinafter in connection with Figure 7. In response to a level of oxygen in exhaust gas flowing through exhaust line 16, oxygen sensor 18 provides an oxygen

signal to control circuit 20. And in response to the oxygen signal input, control circuit 20 generates one or more signals to control or adjust the operation of engine 12, which adjustments can include adjusting the fuel/air mixture into engine 12.

5 An oxygen sensor prepared as described herein can also be used in the intake gas stream of a vehicle. Figure 2 is a diagram of a vehicle 40 having a combustion engine 42 employing a sensing system 44. Sensing system 44 includes oxygen sensor 46 positioned in air intake line 48. Oxygen sensor 46 is operably coupled to control circuit 50. Circuit 50 may 10 include a means to provide a driving electric field for application to sensor 46 to generate a voltage offset corresponding to oxygen level. Such driving means are more fully discussed hereinafter in connection with Figure 7. In response to a level of oxygen in the intake gas stream flowing through air intake line 48, oxygen sensor 46 provides an oxygen signal to control 15 circuit 50. Control circuit 50 is responsive to one or more inputs and generates an output signal to control or adjust the operation of engine 42.

When used with combustion engines the inventive oxygen sensor responds to small variations in oxygen levels in the monitored gas stream with sufficient time response and sensitivity to enhance the control and 20 operation of the combustion engine. Furthermore, the sensors function in both heated and non-heated environments for effective sensing of oxygen levels. The sensor can function in non-heated environments, for example, in non-heated intake gas streams and in exhaust gas streams upon initial 25 start up of the engine before the exhaust gas becomes heated. Therefore, the sensors can be used to enhance the control and operation of an engine upon initial startup. Control of engines upon initial start provides particular advantages because that is when the engine operates least efficiently and produces the most pollutants.

It will be understood by those skilled in the art that the sensing 30 systems 14 and 44 including a nonstoichiometric metal oxide electrolyte and driving means prepared according to this invention will have a wide variety of applications besides use with combustion engines, for example,

but not restricted to, life support systems, medical (life support), biological and environmental analysis and process monitoring.

Figure 3 depicts one embodiment of a sensor member 60 prepared according to the present invention. Sensor member 60 includes sensing member 62 deposited on an electrode material 64 formed on substrate 66. A top electrode 68 is formed on sensing member 62. It will be understood by those skilled in the art that a plurality of top electrodes 68 can be formed on sensing member 62. A plurality of electrodes 68 can be coupled to a driving means to enhance detection of the offset voltage with sensor 60 as will be discussed further in connection with Figure 7. The material comprising sensing member 62 can be made of a nonstoichiometric metal oxide material that is operable as a solid-state electrolyte positioned between metal electrodes in the form of a capacitor or an electrochemical cell. Sensing member 62 may be in the form of a thin film that can be grown using controllable film deposition techniques, such as a metallo-organic deposition (MOD) spin-on, PVD (i.e., sputtering or pulsed laser deposition (PLD)), chemical vapor deposition (CVD), or MOCVD.

Figure 4 is a diagrammatic illustration of one method for depositing a graded material 80 on a substrate 82 using PLD. Source target 84 is formed of first region 86 and second region 88. First region 86 includes a first material having a first composition, and second region 88 includes a second material having a second composition different from the first composition. Regions 86, 88 meet at interface 87 which is generally positioned at about a 45° angle relative to vertical axis 92 for the illustrated embodiment. Laser 90 rasters laser beam 91 over surface 94 of source target 86 along path 96 in a boustrophedonic pattern as illustrated. As laser beam 91 scans across target 84, it liberates material from the respective region 86, 88 in the form of a plume 97 that is subsequently at least partially deposited on substrate 82 as graded material 80. It should be appreciated that for each generally horizontal scan of laser beam 91 across target 84, a different amount of material is released from region 86 relative to the amount of material released from region 88 for the illustrated

orientation of interface 87. Correspondingly, material 80 is formed of layers that gradually change in composition relative to the ratio of region 86 material to region 88 material. The temperature of material 80 may be maintained at a level sufficient to promote diffusion for a given layer 5 resulting in a generally homogeneous composition for that layer.

In an alternative embodiment, interface 87 may be differently configured to adjust the ratio for a given scan of laser beam 91 thereacross. Further, in other embodiments, the source target 84 may include more than two differently composed regions to be scanned to 10 provide for other types of compositions.

This deposition process was used in one example to deposit a graded ferroelectric sensing film on a Pt-Ti-SiO₂-Si substrate held at 600°C in 300 mTorr of O₂. The film has been found to be highly (111)-oriented, as determined by x-ray diffraction. For this example, the deposition process 15 employed a source with regions 86 and 88 having the ferroelectric composition of PbZr_{0.75}Ti_{0.25}O₃, PZT (75/25); and PbZr_{0.55}Ti_{0.45}O₃, PZT (55/45), respectively. Regions 86 and 88 were placed adjacent to one another with the interface at a 45° angle to vertical axis 92. A laser beam was then rastered across the target horizontally while its vertical position 20 was incrementally increased after each horizontal scan as shown by path 96. For each horizontal scan that the laser beam contacted the first and second regions of the target 84, either the first or second composition or both were deposited on substrate 82. Initially, a layer of PZT (55/45) was deposited on substrate 82. During the next scan, the laser beam released 25 an amount of PZT (75/25) as well as an amount of PZT (55/45) from the target source. The relative amounts of PZT 75/25 and PZT 55/45 released from the target for each horizontal scan and deposited on the substrate were substantially equivalent to the amount of each region, 86 and 88, scanned by the laser beam. With each successive scan, the amount of 30 PZT (55/45) deposited became less, while the amount of PZT (75/25) deposited became greater, ending with a final layer of PZT (75/25). For

this example, a total of 15 horizontal scans on the target were performed resulting in a film having a thickness of about 0.3 μm .

For convenience, films with Zr/Ti ratios varying from PZT (75/25) at the substrate to PZT (55/45) at the top surface will be referred to as "up-graded" films. Films with the opposite gradient, i.e. with Zr/Ti ratios varying from PZT (55/45) at the substrate to PZT (75/25) at the top surface, will hereafter be referred to as "down-graded" films. Using the method described above both up-graded and down-graded films can be deposited on substrates.

Both graded and non-graded sensors contain electrodes. A first or "bottom" electrode is formed on the substrate with a small section of the substrate is masked off during deposition to allow access to the bottom electrode. A second or top electrode, is formed via photolithography and sputtering or any other patterning techniques according to procedures well known to those skilled in the art. Materials useful as electrodes, including, for example, platinum, silver, gold, metal phthalocyanine and other conductive metal oxides such as indium-doped tin oxides (ITO) can be used to prepare electrodes. In one example, this second electrode was provided in the form of a number of 50 μm x 50 μm platinum pads. For this example, the resulting sensing structure was like that shown in Figure 3 except for the presence of multiple top electrode pads.

In this manner a compositionally graded sensor element can be prepared at a temperature sufficiently low to be suitable for silicon-based substrates. Correspondingly, processing techniques developed for silicon substrates for use in other applications, such as semiconductor microstructures, may be utilized. The method also obviates the need to interdiffuse successively applied layers each having a compositionally different ferroelectric material.

The relative Zr/Ti concentration of the gradient films as a function of depth is determined using a combination of Auger electron spectroscopy and ion milling to construct a depth profile. X-ray diffraction was used to determine crystalline structure and orientation of the films.

Figure 5 shows the results of Auger depth profiling. The resulting plot is the relative concentration of Zr and Ti as a function of depth for a typical down-graded film prepared as described in connection with Figure 4. The depth profile indicates that the deposition method produces smooth, 5 linear composition gradients, either from PZT (75/25) to PZT (55/45), or vice versa. X-ray diffraction measurements are also consistent with the presence of a range of compositions in the films rather than discrete layers of PZT (55/45) and PZT (75/25).

Figure 6 is a plot of the x-ray diffraction measurements of the (200) 10 peak of an up-graded film prepared as described in connection with Figure 4 along with the (200) peaks for non-graded Zr/Ti 55/45 and Zr/Ti 75/25 films. It is known that the positions of the x-ray peaks for PZT shift with composition. This is evidenced by the two distinct peaks from 55/45 at $2\theta = 44.65^\circ$ and 75/25 at $2\theta = 44.15^\circ$. The peak from the graded film, 15 however, is broad and centered at $2\theta = 44.45^\circ$, which is consistent with a film having a range of compositions between PZT (55/45) and PZT (75/25). Naturally, in other embodiments, oxygen sensors in accordance with the present invention may be manufactured using other processes and techniques as would occur to those skilled in the art.

Figure 7 depicts a schematic of a Sawyer-Tower circuit 110 coupled 20 to an oscilloscope 112. Circuit 110 includes an electrical energy source 114 in the form of a variable voltage supply that generates a frequency adjustable time varying voltage, preferably sinusoidal in nature. Circuit 110 includes a nonstoichiometric metal oxide sensor of the present invention 25 such as a ferroelectric PZT or other type, which is schematically represented as sensor capacitor 115 (C_s). Circuit 110 also includes reference capacitor 117 (C_{ref}) in series with capacitor 115. The time varying voltage from source 114 is applied across the series of capacitors 115, 117, providing a corresponding periodic time varying electric field to 30 drive capacitor 115. The electric field has a peak amplitude or magnitude of at least 1 volt per μm . The peak magnitude of the electric field is more preferably in a range of about 1 to about 1000 volts per μm , and still more

preferably is in a range of about 10 to about 100 volts per μm . A most preferred range of the electric field is about 20 to about 50 volts per μm peak to peak amplitude.

A sinusoidal driving electric field applied to sensor capacitor 115 by circuit 110 generates a hysteretic polarization and an offset voltage. The driving voltage (E_{drive}) generated by source 114 is connected to the x-input of oscilloscope 112 while the voltage across the reference capacitor 117 (C_{ref}) is amplified by amplifier 116 and connected to the y-input of oscilloscope 112. In an ideal system the polarization on the sensor capacitor C_s is proportional to the voltage on the reference capacitor (i.e., sample charge, Q , is equal to the reference capacitor charge, Q_{ref}). In graded and non-graded films, however, a voltage develops across the film leading to voltage across the sensor capacitor 115 (C_s) that is equal and opposite to the voltage across the reference capacitor 117 (C_{ref}).

Circuit 110 was utilized to test the response of various PZT materials with non-graded or graded structures to various mixtures of N_2 and O_2 gases. This response was measured as offset voltage vs. time, t . The ambient oxygen partial pressure, $p(\text{O}_2)$, was controlled via two mass-flow controllers that determined the ratio of N_2 , (or Ar gas) and O_2 entering the chamber. Each particular gas mixture was allowed to flow through the chamber for one hour, at which point a driving electric field at 1 KHz was applied. The subsequent offset voltage was measured as a function of time. This was done using the following N_2/O_2 ratios: (100/0); (95/5); (90/10); (80/20); (50/50); and (0/100).

Reported measurements were performed using a specimen stage comprised of an atmosphere and temperature controlled probe station to allow voltage measurements at ambient temperature. Figure 8 is a diagram of a atmosphere and temperature controlled probe station 150 including sample stage 152 that is a combination resistive heater and Joule-Thompson refrigerator enclosed within sealed housing 154. Sensor 153 is positioned on sample stage 152. Housing 154 includes inlet ports 156 and 158 and exit ports 160 and 162. Oxygen from source 164 flows

through line 166 into mass flow controller 168 and then through line 170 to inlet port 158 of housing 154. Nitrogen from source 172 flows through line 174 into mass flow controller 176 and then through line 178 into inlet port 156 of housing 154. Exit port 160 is connected to a vacuum pump (not shown), and exit port 162 is connected to a bypass valve (not shown).
5 Probes 180 and 182 connect an oxygen sensor to the power supply of the Sawyer-Tower circuit (not shown) inside probe station 150. The system includes two mass flow controllers, 168 and 176, which regulate the flow of different gases from sources 164 and 172 into station 150. The mass-flow controllers were calibrated using a commercial zirconia oxygen sensor. In 10 one operation mode to allow voltage measurements at ambient pressure, the gases in station 150 flow out exit port 162 through a bypass valve (not shown). In alternative operation modes at reduced pressure, exit port 162 is closed and gases inside station 150 are removed through exit port 160. 15 In yet another operation mode, an oxygen sensor is mounted on a stage 152 that is a combination of a resistive heater and a Joule-Thompson refrigerator. This allows measurements to be performed at temperatures from 77K to 580K.

20 Figure 9a is a plot of the voltage offset as a function of time for a non-graded ferroelectric film. The time dependence of the voltage offset, $V_{off}(t)$ has the characteristic shape of a capacitor charging up through a resistance. By varying 117 (C_{ref}) and the amplifier 116 in the Sawyer-Tower circuit, it was determined that the time constant, τ , for the time 25 dependence of V_{off} is approximately equal to $C_{ref}R_{in} = 10$ s. Voltage offsets with this type of time dependent behavior measured using the Sawyer-Tower circuit have previously been shown to be a direct result of an equal and opposite voltage that develops on the sample capacitor. Furthermore, the voltage offset develops only when the driving field is applied, the effect 30 is not observed when the applied field is zero. Figure 9b shows the driving field, E_{drive} , dependence of voltage offset, V_{off} . Below a field, E_{min} , V_{off}

increases monotonically with the driving field. Above E_{min} , V_{off} displays a power law dependence on the driving field.

Figure 10a shows the offset voltage as a function of oxygen concentration measured in various combinations of O_2 and N_2 gas at room 5 temperature using a 1 kHz, to 50 V/ μ m driving field for a non-graded PZT film. A strong dependence of voltage offset on oxygen partial pressure is observed. Figure 10b shows the offset voltage as a function of the oxygen pressure inside the probe station 150 after it was flushed with oxygen gas and pressurized with oxygen at varying absolute pressures. In both cases 10 the magnitude of offset voltage translates to lower d.c. voltage values as the oxygen pressure decreases. The magnitude of V_{off} increases dramatically as the ambient pO_2 is reduced.

Figure 10c shows the voltage offset as a function of temperature. The voltage offset persists over a wide range of temperatures. In preferred 15 embodiments, a non-graded PZT film develops a d.c. voltage offset when subjected to a sinusoidal driving field over a temperature range from about 180K to about 450K for a non-graded PZT film. Correspondingly, the non-graded PZT film for this example has an effective operating range that at least extends between about 180K and about 450K. More preferably for 20 this example, the non-graded PZT film has an effective operating range at least between about 180K and about 400K; and still more preferably between about 180K and about 375K; where effective operating range is understood to mean that the film provides a significant, measurable d.c. voltage offset in response to an applied electric driving field.

25 In another form, the present invention includes a compositionally graded ferroelectric device prepared according to the method depicted in Figure 4. The compositionally graded ferroelectric devices exhibited similar characteristics under the influence of a periodically time varying driving electric field. The compositionally graded PZT film develops a d.c. voltage offset under the influence of the field. Figure 11a is a graph plotting the d.c. voltage offset observed as a series of hysteresis loops as a function of 30 the applied sinusoidal driving field for an up-graded PZT film. Figure 11b is

a corresponding plot for the down-graded film. The direction of the voltage offset depends on the direction of the gradient with respect to the substrate. For the up-graded film, application of a non-zero driving field provide hysteresis loops that reach an equilibrium offset after a few seconds. The 5 hysteresis loops for the up-graded film translate in a positive d.c. voltage direction while those for the down-graded film translate in a negative d.c. voltage direction when the applied sinusoidal driving field is increased. The hysteresis loops measurements were made using the Sawyer-Tower circuit depicted in Figure 7 using a 1 kHz driving field that was varied from zero to 10 50 V/ μ m.

Compositionally graded devices exhibit results similar to those observed for non-graded devices when subjected to various combinations of O₂ and N₂ gas at room temperature and a 1 kHz, 30 V/ μ m driving field for the up-graded films. Figure 12 shows the relationship between the 15 offset voltage as a function of Log[pO₂/atm] with a driving field of 1 kHz, 35 V/ μ m at 300K for up-graded and down-graded films. The plot indicates that the magnitude of the voltage offset depends on the ambient oxygen partial pressure. The offset voltage monotonically increased as the oxygen pressure in the chamber increased.

20 Figure 13 shows the offset voltage as a function of temperature for an up-graded PZT thin film in the temperature range 300K < T < 400K. Offset voltage was observed to monotonically increase as the temperature increased. Furthermore, a significant response was detected at ambient and sub-ambient temperatures. The voltage offset for a graded PZT film 25 persists over a wide range of temperatures. The d.c. voltage offset for a graded PZT film can be observed as low as 400K, or 375K, and even as low as 300K or lower. Thus the graded PZT film may preferably be used for sensing at temperatures below about 400K. More preferably, sensing may be in a range between about 300K and about 400K.

30 In yet another form, the inventive oxygen sensor includes an oxygen deficient ionic oxide material. One example of an oxygen deficient ionic oxide is yttria stabilized zirconia (YSZ). In one example, the YSZ films

were fabricated using pulsed laser deposition on Pt-Ti-SiO₂-Si substrates held at 600 °C in 50 mTorr of O₂. The YSZ material has the composition of Y_xZr_{1-x}O₂, where x is in the range of 0.0 to 0.15. In a preferred form, YSZ film has the composition of Y_{0.06}Zr_{0.94}O₂. The YSZ films were prepared to 5 be approximately 0.8 µm thick and preferentially (111)-oriented as determined by x-ray diffraction.

Figure 14 shows the results of the measurement of V_{off} at 300 K in different pO₂ environments with an applied electric field of 19 V/µm at 100 kHz. For atmospheres of Log[pO₂/atm] ~ 0 to -1, a small (~ 0.1 mV) 10 positive voltage offset was observed which decreased with decreasing pO₂. As Log[pO₂/atm] was reduced below ~ - 0.5, an increasingly negative voltage offset was observed with the largest magnitude of ~ -1.4 mV occurring at Log[pO₂/atm] ~ -3, the lowest pO₂ value tested in this example.

Figure 15 is a graph plotting -V_{off} as a function of the driving 15 frequency and shows the frequency response of a typical sample capacitor driven with a 19 V/µm applied field in an atmosphere of Log[pO₂/atm] ~ -3. The maximum response was observed to occur at a driving frequency of approximately 300 kHz. The magnitude of the voltage offset also increased exponentially with the amplitude of the applied electric field.

20 Correspondingly, the YSZ film can be used at temperatures below about 300K to sense oxygen. The resulting sensor may be quite small, and it requires no reference gas, making it suitable for biomedical applications (among others).

Any publications, patents, or patent applications cited herein are 25 hereby incorporated by reference as if each publication, patent or patent application were set forth in its entirety herein. The citations incorporated by reference include the following:

While the invention has been illustrated and described in detail in the drawings and foregoing description, the same is to be considered as 30 illustrative and not restrictive in character, it being understood that only the preferred embodiment has been shown and described and that all changes and modifications that come within the spirit of the invention are desired to

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be protected. Further, any theory of operation, proof, or finding stated herein is meant to further enhance understanding of the present invention and is not intended to make the scope of the present invention dependent upon such theory, proof, or finding.